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<b>(54) Title:</b> QUATERNARY AMMONIUM SALT COMPOSITIONS, AND METHODS FOR TREATING SUBSTRATES  <b>(57) Abstract</b> <p>The present invention is directed to compositions and methods for treating and preserving substrates, such as cellulosic materials, such as wood or plant fibres. Water insoluble biocidal compositions comprising a biocidally effective amount of a biocide formed by mixing a first biocidal compound which is a quaternary ammonium salt having the formula <math>R^1R^2R^3R^4N^+X^-</math> wherein <math>R^1</math> and <math>R^2</math> are independently straight, branched, or cyclic alkyl groups 8 to 18 carbon atoms, and <math>R^3</math> and <math>R^4</math> are independently straight alkyl groups having 1 to 7 carbon atoms or branched or cyclic alkyl groups having 3 to 7 carbon atoms, and <math>X^-</math> is an anion and a second biocidal compound selected from the group consisting of alkali and ammonium salts of dialkyldithiocarbamate, monoalkyldithiocarbamate, tetrafluoroborate, and hexafluorophosphate, wherein said composition has a water solubility lower than that of said first biocidal compound are applied to the substrates as an antifungal and antimicrobial treatment. These compositions provide significant improvement over the commercial control, didecyldimethylammonium chloride, with regard to resistance to leaching. As a result, the compositions and methods of the invention are particularly suitable for treating wood to be used in an exterior environment.</p>		

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## QUATERNARY AMMONIUM SALT COMPOSITIONS, AND METHODS FOR TREATING SUBSTRATES

### BACKGROUND OF THE INVENTION

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#### 1. FIELD OF THE INVENTION

This invention is directed to compositions containing biocidal quaternary ammonium salts and to a method for treating substrates to protect them from fungal or microbial attack by contacting or impregnating the substrates with these compositions. In particular, the invention is directed to an antifungal treatment compositions for fibrous materials or wood and to methods for providing these materials with antifungal properties by treating with the quaternary ammonium salts of the present invention.

#### 2. DISCUSSION OF THE RELATED ART

Many naturally occurring cellulosic or lignocellulosic materials, e.g., wood and other fibrous materials, are known to be susceptible to attack and eventual destruction by microorganisms, particularly by various fungi. Such attack is particularly likely where the wood or fibrous material is exposed to the elements or comes into contact with the soil (such as wood that is used in exterior construction or decorative uses, such as outdoor patios or decks), or is exposed to a moist environment (such as fibers used in air purification filters, carpeting, clothing, etc.). As a result, it is desirable to provide these materials with biocidal (in particular with fungicidal) properties to provide them with decay resistance.

In addition to the attack and destruction of the fibrous, naturally occurring materials discussed above, synthetic materials, such as plastics or synthetic fibers, can also provide a substrate for the growth of microorganisms. When plastics, or synthetic or naturally occurring fibers are used in a health care setting or other setting requiring control or avoidance of the presence of microorganisms (in particular of pathogenic microorganisms which can result in the spread of disease) it is desirable to provide these materials with resistance to such microbial growth, e.g. by incorporating or coating the fiber or plastic with a biocide.

The biological activity of alkylamines, where some or all of the alkyl groups are long chain aliphatic groups ( $C_8$  and larger), is well known. However, quaternary ammonium salts, which are positively charged nitrogen atoms covalently bound to four substituents and ionically bound to a counter-ion, have been found to be especially biocidally active.

- 5 Quaternary ammonium salts are usually characterized by their broad spectrum biocidal activity against both gram-positive and gram-negative microorganisms. Their uses range from algacides for water treatment to bacteriostats in consumer products such as shampoos and disinfectants. Quaternary ammonium salts are typically secondary or tertiary amines which have undergone methylation with methyl chloride, such that the quaternary ammonium  
10 chloride salt is obtained. One example of a quaternary ammonium chloride salt known and approved for use as a biocide in the pressure treatment of wood is didecyldimethylammonium chloride (DDAC).

- Since the quaternary ammonium salts are cationic, reactions with anionic substances can occur. For example, hydroxyl groups of materials such as cotton or cellulose can react  
15 with the ammonium action, which replaces the hydrogen ion to form strong bonds with these materials. However, in many cases the reaction of the quaternary ammonium action with hydroxyl groups is undesirable. The interaction of typical quaternary ammonium salts with cellulose causes poor penetration of the biocide when used in the pressure treatment of wood (Walker, Leigh E., "Alkylammonium Compounds as Wood Preservatives," Forest Product  
20 Society Meeting, Savannah, Georgia, September 26 - 28, 1994). This interaction is illustrated by steep gradient profiles of the biocide in treated wood, and strong selective adsorption of the preservative. In addition, the reaction is frequently reversible under the conditions of exposure to soil or to a water leaching environment (Archer, Kevin, L. Jin, A. F. Preston, M. G. Richardson, D. B. Thies, and A. R. Zahora, "ACQ - Proposal to the American Wood  
25 Preservers Association Treatments Committee," 1993).

Another potential problem with using certain quaternary ammonium salts, in particular quaternary ammonium chlorides, is the associated corrosion caused when aqueous chloride ions come into contact with carbon steel vessels or equipment, or with carbon steel fasteners in contact with wood or fibrous material impregnated therewith.

- 30 Because of the above disadvantages, it would be advantageous to have a fungicidal or microbicidal composition containing quaternary ammonium salts that are relatively insoluble

in water, that yield a consistent biocide distribution throughout the substrate treated therewith, and that exhibit low leachability upon exposure to the elements and that do not result in process equipment or fastener corrosion.

Another class of compounds known as biocides in the pressure treatment of wood are the dialkyldithiocarbamates. In particular sodium dimethyldithiocarbamate is approved for this use. However, dithiocarbamate compounds, are also very water soluble, and lead to similar leaching problems when used as biocides.

Similarly, tetrafluoroborate and hexafluorophosphate compounds are also very water soluble, and would be expected to exhibit similar leaching behavior if used as biocides.

### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a biocidal composition containing a quaternary ammonium salt that imparts microbicidal and/or fungicidal properties to a substrate, such as wood or other cellulosic materials, without the problems associated with the aqueous solubility of individual biocidal salts.

It is also an object of the present invention to provide a biocidal composition prepared from two biocides approved for the pressure treatment of wood, in a form that is relatively insoluble, thereby increasing the retention of the biocide in the substrate, achieving a more even distribution profile of biocide throughout the substrate, and a less acidic treatment solution.

The objects and advantages discussed above, as well as other objects and advantages, are provided by the present invention, which is directed to biocidal compositions formed by combining a first biocidal compound, which is a quaternary ammonium salt, with a second biocidal compound, which is a salt of an anion selected from the group consisting of tetrafluoroborates, dialkyldithiocarbamates, monoalkyldithiocarbamates, and hexafluorophosphates, together with a suitable carrier. More specifically, the present invention is directed to compositions formed by combining a first biocidal compound which is a quaternary ammonium salt having formula



wherein  $R^1$  and  $R^2$  are straight, branched, or cyclic alkyl groups having 8 to 18 carbon atoms, and  $R^3$  and  $R^4$  are straight alkyl groups having 1 to 7 carbon atoms, branched alkyl groups

having 3 to 18 carbon atoms, or aralkyl groups having 7-18 carbon atoms, and X<sup>-</sup> is an anion, such as a halogen anion, with a second biocidal compound, which is a salt, such as an alkali metal salt or an ammonium salt, of a compound selected from the group consisting of dialkyldithiocarbamate, monoalkyldithiocarbamate, tetrafluoroborate, and

5 hexafluorophosphate. While not wishing to be bound by any theory, the inventors believe that the first biocidal compound and the second biocidal compound form a salt or complex that is relatively insoluble in water, and is somewhat soluble in organic solvents.

Typically, the quaternary ammonium salts of the first biocidal compound of the compositions of the present invention contain two large alkyl, cycloalkyl, or aralkyl groups  
10 (i.e., having 8 to 18 carbon atoms) and two small alkyl or cycloalkyl groups (i.e., having 1 to 7 carbon atoms), for a total of four substituents. When the second biocidal compound contains a dialkyldithiocarbamate, the alkyl groups desirably have between 1 and 10 carbon atoms. A composition formed by combining a didecyldimethylammonium halide with an alkali metal salt of dimethyldithiocarbamate is particularly suitable with respect to its ability  
15 to resist leaching, as well as its biocidal activity, e.g., its ability to prevent or decrease fungal decay.

The present invention is also directed to treated substrate compositions containing a substrate, to which it is desired to impart microbicidal or fungicidal properties, and one or more of the biocidal compositions described above. For instance, the substrate may be a  
20 cellulosic material, such as wood or plant based fiber, such as cotton or jute, or may be a synthetic material or fiber, such as carpet fibers, or may be a fabric made from these fibers. The substrate may be an object made from plastic or other material and having surfaces or areas to which it is desired to impart biocidal properties. As an example, the substrate may be any surface or material which is conventionally treated with biocide compositions, in  
25 particular with quaternary ammonium salt biocide compositions.

As pointed out above, the compositions of the present invention may also contain a carrier, solvent, adjuvant or auxiliary suitable for application to a surface, for mixing with a liquid, or for impregnation into a solid. As pointed out above, an advantage of the composition of the present invention is that it is relatively insoluble in water, particularly as  
30 compared to didecyldimethylammonium chloride alone. This allows the formulation of compositions that can be administered in ways that will increase their penetration into the

substrate without immediately bonding to, or undergoing ion exchange with, the substrate material.

The composition may be used in the form of an emulsion or suspension, e.g., an oil-in-water (O/W) emulsion of the mixture of the two biocidal compounds, e.g. in an organic solvent solution of the mixture. For example, the compositions of the present invention could be formulated as emulsions containing, e.g., a polyquaternary ammonium compound (e.g., a polyquaternary compound based upon polyamines and polyamine ethers, polyvinyl pyrrolidones, polyquaternary ammonium polymers, or cationic polymers based on acrylates), thickening or dispersing agents (e.g., homopolymers or copolymers of (meth)acrylic acids and esters, vinyl homopolymers and copolymers, and polymers based on glycol monomers and on ether monomers), and nonionic surfactants (such as polyalkoxylates of alkylphenols, alcohols, amines, and alkanolamides, or block polymers of ethylene and propylene oxides). Emulsions of this type are disclosed in U.S. Patent 5,112,396, which is hereby incorporated by reference.

The compositions of the present invention may be used to coat or impregnate a variety of substrate articles, such as textiles or fabrics, fibers, plastics, consumer articles, etc., or may be combined with conventional ingredients to form further compositions, such as paint compositions (e.g., oil based paint, latex based paint), coating compositions, plastic compositions, fibers (e.g., for carpeting or textiles), consumer products compositions (e.g., shampoos, household cleaners), or other compositions where biocidal or biostatic activity is desirable. In particular, the present invention is directed to compositions for the treatment and/or preservation of wood or other cellulosic products, more particularly, to compositions for the preservation of wood, fiber, fabric, cardboard, paper products, or other cellulosic products from fungal or other biocidal attack.

The present invention is also directed to methods for treating substrates to impart biocidal properties thereto by applying to or impregnating into the substrate an effective amount of the composition of the invention, discussed above. The amount of composition applied will depend upon the formulation thereof, and is that amount which will deliver an amount of quaternary ammonium salt and dithiocarbamate effective to prevent or reduce fungal or other microbial attack. This amount may be equal to or less than that conventionally used for either the quaternary ammonium compound or the second biocidal

compound individually, since the compositions of the present invention exhibit decreased leaching behavior, as discussed below.

A significant and unexpected advantage of treating substrates, such as wood, using the compositions of the present invention as compared to other compositions containing individual quaternary ammonium halide salts or other individual biocides is that the biocides of the present invention are less likely to be leached from the substrate by contact of the substrate with water or other liquid after treatment. Water leaching can be measured, for example, in a manner similar to that described by the American Wood Preservers' Association (AWPA, 1989): "Standard Method of Determining the Leachability of Wood Preservatives" (E11-87). Without being bound by any theory, the present inventors believe that the decreased leachability exhibited by the compositions of the present invention is due to the low water solubility of the biocides when used in the composition of the present invention.

Another significant and unexpected advantage of the present invention is the excellent penetration of the biocides into the substrate, in particular wood or other cellulosic material capable of absorbing the biocides, resulting in a more desirable distribution of the biocides throughout the thickness of the substrate. Again, without being bound by any theory, the present inventors believe that this is due to the relative insolubility of the biocides when applied as the composition of the present invention, allowing for a deeper absorption of the biocides before the occurrence of any binding or ion exchange of the quaternary ammonium biocide with sites inside the substrate, such as cellulosic hydroxy compounds. This leads to yet a third unexpected and significant advantage obtained most commonly when the substrate is wood or other cellulosic material, i.e., the decreased hydrogen ion formation resulting from decreased ion exchange of the quaternary ammonium biocide with cellulosic hydroxy moieties. This results in decreased acidification of the treatment liquid, which in turn decreases the need to neutralize the treatment liquid during reuse, and avoids corrosion of process equipment, as well as corrosion of fasteners that might be used with the treated substrate.

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and



scope of the invention will become apparent to those skilled in the art from this detailed description.

### **DETAILED DESCRIPTION OF THE INVENTION**

5       The compositions of the present invention can be prepared, for example, by combining the quaternary alkylammonium chloride of the first biocidal compound with a sodium or ammonium salt of a biocidal anion of the second biocidal compound, such as a sodium dialkyldithiocarbamate, ammonium tetrafluoroborate, or ammonium hexafluorophosphate. Preparation techniques for both quaternary alkylammonium chlorides  
10      and alkali or ammonium dialkyldithiocarbamates, tetrafluoroborates, or hexafluorophosphates are well known to those of skill in the art. Both didecyldimethylammonium chloride and sodium dimethyldithiocarbamate, for instance, are registered pesticides for the treatment of wood.

15       The compositions of the present invention have biocidal activity, including, but not limited to, antifungal activity and antimicrobial activity. A biocidally effective amount of the compositions of the present invention is an amount sufficient to inhibit or prevent the growth of fungi or other microbes, for at least some period of time, preferably on the order of months or years. Antifungal or fungicidal activity, as these terms are used herein, denote activity (e.g., growth inhibition or prevention) against fungi, including molds, in particular against the  
20      Basidiomycetes fungi which attack wood or other cellulosic material, and may include fungi associated with or causing brown rot (wherein cellulose is attacked preferentially and lignin is left basically unchanged), soft rot, white rot (wherein both cellulose and lignin are decomposed), or combinations thereof. The antifungal activity of the compositions of the present invention can be shown, for example, by exposing treated wood to various wood  
25      destroying fungi, and comparing the results to those obtained when untreated wood is similarly exposed, as discussed below. Antimicrobial or microbiocidal activity, as such terms are used herein, denote activity against microbes or microorganisms different from fungi, such as bacteria, slime molds, protozoa, etc. This activity can be shown, for example by assaying the effect of the compositions of the present invention against microorganisms, as  
30      discussed below.

The term alkyl as used herein, unless otherwise specified, refers to a saturated straight chain hydrocarbon of 1 to 24 carbon atoms, or a branched hydrocarbon of 3 to 24 carbon atoms, including, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, neopentyl, hexyl, isohexyl, 3-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, and decyl. The term cycloalkyl as used herein, unless otherwise specified, refers to a cyclic hydrocarbon of 3 to 24 carbon atoms, including, e.g., cyclopentyl and cyclohexyl.

The term aryl as used herein, and unless otherwise specified, means aromatic hydrocarbyl, and refers to phenyl, naphthyl, or anthranyl, each of which may be unsubstituted or have up to three substituents, wherein each substituent is independently halo or alkyl.

As used herein, the term aralkyl refers to an alkyl group, as defined above, that has an aryl substituent, as defined above. Heteroaralkyl substituents, in which an alkyl group has a heteroaryl substituent, can be used in place of or in addition to aralkyl substituents.

As used herein, the term water soluble refers to a solubility in water of at least about 3% by weight. Water insoluble, as used herein, refers to a solubility in water of less than about 3% by weight.

The compositions of the present invention provide the biocides in a form that is relatively insoluble in water, as compared to the individual biocides alone, and which is somewhat soluble in organic solvents. The compositions of the present invention usually having a solubility of about 5% by weight or more in a polar organic solvent, such as acetonitrile, methylene chloride, and the like. Suitable alkyl substituents for the dialkyldithiocarbamates include those alkyl groups defined above, in particular alkyl substituents having 1 to 8 carbon atoms.

As discussed above, the biocidal compositions of the present invention are formed by mixing a first biocidal compound which is a quaternary ammonium salt biocide which has the following formula



wherein  $R^1$  and  $R^2$  are alkyl, cycloalkyl, or aralkyl groups having 8 to 18 carbon atoms,  $R^3$  and  $R^4$  are alkyl groups having 1 to 18 carbon atoms, cycloalkyl groups having 3 to 18 carbon atoms, or aralkyl groups having 7 to 18 carbon atoms, and  $X^-$  is an anion, such as a halogen anion, with a second biocidal compound containing an alkali metal or ammonium action and

an anion selected from the group consisting of dialkyldithiocarbamates, monoalkyldithiocarbamates,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ .

Also as discussed above, the quaternary ammonium salts preferably have two large alkyl groups (having 8 to 18 carbon atoms) and two small alkyl groups (having 1 to 7 carbon atoms), for a total of four groups. In particular, the quaternary ammonium salt of the first biocidal compound may be didecyltrimethyl ammonium chloride and the second biocidal compound mixed therewith to form the composition of the present invention is desirably sodium dimethyldithiocarbamate.

As mentioned above, the preparation of the compositions of the present invention can be accomplished by mixing the first and second biocidal compounds together using known mixing methods, e.g., in water or other polar solvent. In one embodiment, the compositions are formed by mixing the water soluble first biocidal compound, e.g., didecyltrimethylammonium chloride, with the water soluble second biocidal compound, e.g., sodium dimethyldithiocarbamate, ammonium tetrafluoroborate, etc., in water. Any convenient molar ratio of the first and second biocidal compounds may be used, especially a molar ratio of first biocidal compound to second biocidal compound of 2:1, more especially of 1:1.

Mixing these biocidal compounds results in the formation of an insoluble composition as a viscous liquid, wax, or crystalline solid. This composition is obtained in amounts that range from 75 to 100 percent, based upon the amounts of biocidal compositions mixed together, depending on the particular biocidal compounds mixed together. The resulting compositions are somewhat soluble in organic solvents as mentioned above, particularly polar organic solvents, such as acetonitrile or methylene chloride. Other organic solvents may also be used to form an emulsion of the composition of the present invention, as discussed above.

The invention can be more thoroughly understood by referring to the following non-limiting examples.

#### Example 1

Into a one liter beaker containing didecyltrimethylammonium chloride (90.52 grams of an 80 percent solution by weight, 0.200 moles) in 50 mL water, ammonium tetrafluoroborate (20.96 grams, 0.200 moles) in 50 mL water was added. An additional 60 mL of water was added to the mixture, which was then stirred for one hour. The mixture was

poured into a 500 mL separatory funnel and allowed to stand for 15 minutes, causing separation of a colorless oil. The aqueous layer was removed and the product washed with 100 mL water. After allowing separation of the oil layer and the aqueous layers to occur, which required approximately 1.5 hours, the aqueous layer was removed, and the resulting insoluble biocide composition (85.00 grams, 82.7 %) was collected in a vial. The calculated analysis in weight percents for this composition is: C 63.91; H 11.70; N 3.39; B 2.61; and F 18.38. Found (wt. %): C 63.86; H 11.93; N 3.38, B 2.35; and F 13.88.

#### Example 2

Didecyldimethylammonium chloride (181.0 grams of an 80 percent by weight solution, 0.400 moles) in 800 mL of water was mixed with 144.0 grams (0.202 moles) of an aqueous solution of sodium dimethyldithiocarbamate (40 wt. %). A cream colored solid precipitated immediately. The slurry was stirred for two hours, vacuum filtered, and washed with 150 mL of water. The resulting solids were air dried to constant weight to give a solid yellow product (132.9 grams, 74.4%). The calculated analysis in weight percent for this composition is: C 67.20; H 12.12; N 6.27; S 14.35. Found (wt. %): C 66.91; H 12.26; N 6.28; and S 14.51.

#### Example 3

In a two liter beaker, didecyldimethylammonium chloride (181.1 grams of an 80 percent by weight solution, 0.400 moles) and sodium diethyldithiocarbamate (90.12 grams of a 40 percent by weight solution, 0.400 moles) were mixed together. The mixture was stirred for one hour. The resulting dark brown oil was separated from the aqueous phase and dried over Drierite to yield 214.7 grams of a dark brown oil. The calculated analysis in weight percent for this composition is: C 68.29; H 12.31; N 5.90; S 13.50. Found (wt. %): C 60.89; H 12.56; N 4.91; S 10.77.

#### Example 4

Didecyldimethylammonium chloride (181.0 grams of 80 weight percent solution, 0.4 moles) in 800 mL water was mixed with sodium di-n-butylthiocarbamate (196.0 grams of a 46.4 percent by weight solution, 0.400 moles). The resulting dark brown oil was separated

from the aqueous phase, washed with 200 mL water, and dried over Drierite. The calculated analysis in weight percent for this composition is: C 70.39; H 12.19; N 5.30; and S 12.12. Elemental analyses found (wt. %): C 63.83; H 12.32; N 4.38; and S 8.94.

5           **Example 5**

In a 500 mL beaker, 45.2 grams (0.100 moles) of didecyldimethylammonium chloride in 100 mL of water was mixed with 16.60 grams of ammonium hexafluorophosphate in 100 mL of water. While a white solid formed immediately upon mixing of the two reagents, the mixture was nevertheless stirred for about one hour. The solids were vacuum filtered and air  
10       dried to constant weight to give a white solid. The calculated analysis in weight percent for this composition is: C 56.03; H 10.26; N 2.97; P 6.57; and F 24.17. Found (wt. %): C 53.84; H 10.41; N 3.88; P 4.99; and F 19.06.

**Example 6**

15           An aqueous solution of benzalkonium chloride (a quaternary ammonium chloride consisting of a benzyl group, two methyl groups, and a long chain alkyl group ranging from C<sub>8</sub> to C<sub>18</sub>) (56.76 grams) was dissolved in 200 mL of water. Ammonium tetrafluoroborate (20.96 grams 0.200 moles) was added. While white solids separated immediately, the mixture was nevertheless stirred for one hour. The solids were vacuum filtered, washed with  
20       water, and air dried to constant weight to give 33.1 grams of a white solid. The calculated analysis in weight percent for this composition is (for R = C<sub>14</sub>H<sub>29</sub>): C 65.89; H 10.09; N 3.34; B 2.57; F 18.11. Found (wt. %): C 64.22; H 10.13; N 3.48; B 2.31; F 14.12.

**Example 7**

25           Benzalkonium chloride (129.57 grams of a 50% aqueous solution) was diluted with 200 mL water. Sodium dimethyldithiocarbamate (112.07 grams of a 40 percent by weight aqueous solution, 0.313 moles) in 200 mL of water was added. The mixture was stirred for one hour. The resulting yellow oil was separated and recrystallized from methylene chloride to yield 36.52 grams of a white solid. The calculated analysis in weight percent for this salt  
30       is: C 67.23; H 11.28; N 6.53; S 14.95. Found (wt. %): C 64.78; H 12.57; N 5.20; S 14.03.

**Example 8**

Benzyltrimethylammonium chloride (18.6 grams, 0.100 moles) in 50 mL of water was combined with a solution of ammonium tetrafluoroborate (10.5 grams, 0.100 moles) in 50 mL water. White solids formed immediately. After stirring the mixture for one hour, the solids were filtered, washed with water, and air dried to constant weight to yield a white solid. The calculated analysis in weight percent for this salt is: C 50.67; H 6.80; N 5.91; B 4.56; F 32.06. Elemental analyses of these solids found (wt. %): C 50.38; H 6.87; N 5.87; B 4.45; F 27.42.

**Example 9**

Triptentylamine (5.70 grams, 0.0243 moles) in 32 mL water, was combined with 25.3 mL of 0.1 N hydrochloric acid. Ammonium hexafluorophosphate (4.08 grams, 0.025 moles) was added to the solution, causing solids to separate. The slurry was stirred for one hour and the resulting solids were filtered, washed with water and air dried to provide (8.58 grams of a wax-like solid). The calculated analysis in weight percent for this composition is: C 48.25; H 9.18; N 3.75; P 8.29; F 30.53. Found (wt. %): C 49.19; H 9.63; N 3.91; P 6.77; F 23.85.

As mentioned above, the biocides of the present invention can be used in compositions that provide antifungal or antimicrobial properties to a substrate incorporated or treated therewith, e.g., in compositions for antifungal treatment of wood and other lignocellulosic or cellulosic materials, or in compositions for use in sanitizing other substrates, such as floors, carpets, countertops or other surfaces, etc. Due to their decreased water solubility relative to other, individual, biocides, the compositions of the present invention are less likely to leach out of or wash off of the substrate under conditions of use, especially under conditions where the substrate is exposed to the elements, e.g., in outdoor uses, or is exposed to contact with aqueous solutions, e.g., in a hospital or other environment. The compositions of the present invention can be formulated into a solution (in organic solvents), a suspension, or an emulsion, and impregnated into a substrate under pressure and pH conditions known in the art for impregnating wood with didecyldimethylammonium chloride (DDAC). These conditions can be varied in accordance with methods known in the art for use with DDAC in order to obtain a desired retention of the biocide of the present

invention. "Retention" is defined, for purposes of this invention, as the amount of biocide absorbed per unit volume of substrate or wood, prior to any leaching testing. For instance, the initial air pressure or vacuum method, the empty cell method, the modified full cell method, the full cell method, or the refusal method, as described in AWP Standard (1994)

5 C1-94, can be used.

More particularly, a vacuum impregnation method can be used wherein the wood or other cellulosic material to be treated, which may be weighted, is placed in a pressure vessel, which is then evacuated. The material is allowed to remain in the evacuated vessel for a period of time, usually around 1 hour. A treating solution, suspension, or emulsion  
10 containing a composition of the present invention is then allowed to enter the pressure vessel (still under vacuum) until the vessel is about 2/3 to 3/4 full. The substrate is totally immersed in the solution, and is then subjected to a pressure of around 100 to 200 psi for a period of time, usually about an hour. The pressure and treatment time may be varied depending on the type of substrate, the thickness or shape of the pieces, etc. After the treatment time has  
15 elapsed, the substrate is removed from the vessel, allowed to drain, and weighed, so that the solution retention can be calculated. The substrate can then be dried and used as is known in the art for treated substrate, such as for treated wood or lumber.

Alternatively, the solutions, suspensions, or emulsions containing the compositions of the present invention can be sprayed or otherwise coated onto the surfaces of the substrate,  
20 and any solvent present allowed to evaporate, according to methods known in the art for applying biocidal compositions to objects or materials.

**WATER LEACHING OF TREATED WOOD**

A particular substrate of interest is wood. The present inventors have found that the biocides for use in preservatives for wood (or other substrates) desirably have low water solubility, particularly when the wood is intended for exterior use, in order to prevent or  
5 minimize leaching of the preservative by rain or other water or aqueous solutions, which can both decrease the resistance of the wood to decay and contaminate the resulting leachate water with biocide. Thus, low water solubility is very desirable in biocidal preservative compounds to be impregnated in, or coated on, wood or other substrates. The present inventors have found that the composition of the present invention provides a biocide that  
10 exhibits this low water solubility, a result that is surprising in view of the water solubility of DDAC. To illustrate this, testing of several of the biocidal compositions of the present invention was performed by impregnating the wood with a composition prepared by dissolving the biocide composition of the present invention in an organic solvent, such as methylene chloride. Similarly, compositions of the present invention could be formulated  
15 into, and applied as, an aqueous emulsion using commercially available emulsifiers.

Water leaching tests were performed on wood treated with a biocidal compositions prepared according to Examples 1, 2, and 5. The tests performed were similar to the test described by the American Wood Preservers' Association (AWPA) in "Standard Method of Determining the Leachability of Wood Preservatives" (E11-87). The AWPA method  
20 involves the use of six 3/4 inch blocks of treated wood, which are impregnated with water prior to the leaching process. The blocks are submerged in 300 mL of water, which is agitated by magnetic stirring. The water is exchanged for fresh water at various time intervals (6, 24, 48, etc. hours) and the leached chemical is quantified by the appropriate analytical procedure. The leaching study used four 3/4" blocks, treated to a 0.20 pcf (8.0  
25 kg/m<sup>3</sup>) retention, and 230 mL of leaching water per time interval. The study was done in duplicate.

The results obtained are described in Table 1 below as percentages of total biocide loaded that were leached at the various time intervals, as well as the total amount leached. The leachate was analyzed by inductively coupled plasma (ICP) spectroscopy. The  
30 dimethyldithiocarbamate concentration was determined by measuring sulfur content; the hexafluorophosphate concentration was determined by measuring phosphorus content, and



the tetrafluoroborate concentration was determined by measuring boron content. For this study, the concentration of the didecyldimethylammonium ion was not directly measured.

TABLE I

Water Leaching of Biocide Compositions.\*

Time, hrs.	Biocide of Example 1	Biocide of Example 2	Biocide of Example 5
21	7.20	1.33	15.28
45	6.38	1.31	8.89
93	6.00	1.67	9.29
165	7.48	1.13	9.34
237	8.10	1.15	7.48
285	7.14	1.07	NA
Total Leached	42.3	7.70	50.3

\*Values in percent. Gauge retention (i.e. treating data) was used to calculate initial chemical in blocks.

The leaching of didecyldimethylammonium chloride (DDAC) treated wood has been reported by Ruddick and Sam (Ruddick, J. N. R., and A. R. H. Sam,

"Didecyldimethylammonium Chloride - A Quaternary Ammonium Wood Preservative: Its Leachability from, and Distribution in, Four Softwoods". Material and Organismen, 17, 299 -

313 (1982)) to be in the 10 to 20 percent range for Hem-fir treated to retentions of 1.88 to

2.19 pcf (30 to 35 kg/m<sup>3</sup>). Later studies by Walker (Walker, L. E., "Didecyldimethyl-

ammonium Chloride. DDAC, Wood Preservatives. Information Update for the P-3

Preservative Committee of the American Wood Preservers' Association", (1994)) have shown

that water leaching caused between 40 and 70 percent of the DDAC to be depleted for low

retentions, i.e. 0.05 to 0.063 pcf (0.8 to 1.0 kg/m<sup>3</sup>), and less than 10 percent leached for

retentions greater than 0.063 pcf (1.0 kg/m<sup>3</sup>).

The leaching results for the biocide of Example 2 at 0.20 pcf (8.0 kg/m<sup>3</sup>) is somewhat lower than that obtained for DDAC. While the overall results for the for the biocides of Examples 1 and 5 are considerably higher than those reported in the literature for DDAC at these retention levels, examination of the leaching data shows that the levels of each of the

quaternary ammonium salts of the present invention leached during every leaching time interval are approximately consistent or constant. This is not true with other, individual biocides, such as DDAC, which typically exhibits a large release of chemical followed by smaller amounts over time. The leaching data strongly suggest that the solubility or

5 solubility product of the biocide composition is an important parameter for leaching. Review of the leaching data shows that the biocide composition of Example 2 produces a leachate solution containing about 2.0 ppm sulfur, the biocide composition of Example 5 produces a solution containing about 4.5 ppm phosphorus, and the biocide composition of Example 1

10 produces a solution containing approximately 6.0 ppm of boron for each time interval. Using these quantities and assuming the didecyldimethylammonium species is also leached at the same level, the solubility products ( $K_{sp}$ ) can be obtained, and are given below in Table 2.

TABLE 2  
Solubility Product for Didecyldimethylammonium Salts.

	Biocide Composition of Example 1	Biocide Composition of Example 2	Biocide Composition of Example 5
$K_{sp}$	$3.1 \times 10^{-7}$	$9.8 \times 10^{-10}$	$2.1 \times 10^{-8}$

15  $K_{sp} = [\text{quaternary ammonium species}] [\text{second biocidal compound anion}]$

Without wishing to be bound by any theory, it is believed that these relatively small values for the solubility product enable the biocide compositions of the present invention to have good permanence (i.e., low leachability) in exterior applications. At the same time, the

20 salts provide excellent resistance to fungal and bacterial degradation, as shown here.

### **ANTIFUNGAL ACTIVITY**

Fungal testing of three of the biocidal compositions of the present invention was done with wood destroying organisms. These organisms were comprised of brown, white, and soft

25 rot fungi, as well as staining fungi/bacteria. The compounds tested were the same compounds examined for water leaching above.

Fungal testing was conducted at three compound retentions: 0.2, 0.4, and 0.6 pounds per cubic foot (pcf). The treating solution consisted of a methylene chloride solution of the

biocidal compositions of Examples 1 and 2 and an ethanol solution of the biocidal composition of Example 5. Sixteen southern yellow pine (SYP) 3/4 inch blocks were treated to each retention by vacuum impregnation.. Approximately one dozen of these blocks were used, in order to provide meaningful fungal decay data. Prior to efficacy testing, the treated  
5 blocks were water leached according to AWP A E11-87. Untreated SYP blocks were used as controls. Blocks treated with aqueous solutions of didecyldimethylammonium chloride at the above retentions were employed for comparative purposes.

The method used for testing efficacy was a modified AWP A soil block test. The soil used was taken from a field stake test plot in Conley, Georgia, and was used as is, and not  
10 sterilized. The soil was placed in plastic containers (8 x 16 x 30 inches) or tubs, to a depth of approximately four inches. The moisture content was adjusted and maintained at 40 percent. Untreated wafers of southern yellow pine (0.25 x 1.5 x 1.5 inches) were used as fungi feeder strips. The 3/4 inch SYP treated blocks were placed on the feeder strips and the container covered and placed in a constant temperature chamber, which was maintained at 80°F (27°C).

15 Seven tubs were used for this five month, fungal efficacy testing. Although the fungal activity was slightly different from tub to tub, the random placement of the sample blocks permitted averaging of the efficacy rating. Table 3 gives the percent of the sample blocks having no decay, questionable decay, initial or early stages of decay, and decay in the form of either brown, white, or soft rot.

20

**TABLE 3**  
**SOIL BLOCK EFFICACY TESTING OF BIOCIDAL COMPOSITION**  
**VERSUS UNTREATED AND DDAC TREATED CONTROLS\***

Untreated Control	0.0	0.0	4.0	96.0
Treating Retention: 0.20 pcf (3.2 kg/m <sup>3</sup> )				
Biocidal Composition	No Decay	Questionable	Initial Decay	Decay
DDAC	0.0	8.3	75.0	16.7
Example 2	6.3	31.2	56.2	6.3
Example 5	0.0	8.3	66.7	25.0
Example 1	0.0	8.3	75.0	16.7
Treating Retention: 0.40 pcf (6.4 kg/m <sup>3</sup> )				
Quat Salt	No Decay	Questionable	Initial Decay	Decay
DDAC	0.0	0.0	72.7	27.3
Example 2	66.7	33.3	0.0	0.0
Example 5	8.3	8.3	58.3	25.0
Example 1	0.0	0.0	75.0	25.0
Treating Retention: 0.60 pcf (9.6 kg/m <sup>3</sup> )				
Quat Salt	No Decay	Questionable	Initial Decay	Decay
DDAC	0.0	16.7	66.7	16.7
Example 2	43.8	56.2	0.0	0.0
Example 5	0.0	16.7	58.3	25.0
Example 1	0.0	33.3	58.3	8.3

5 \*Values in percent of blocks in the category.

10 The data provided by the modified soil block efficacy testing on water leached blocks can be related to the retention level, as summarized below in Table 4. This Table assumes that questionable decay is essentially no decay. The results indicate that the salts of the present invention perform as well as, or better than, the didecyldimethylammonium chloride (DDAC) alone. As can be seen from Table 4, the biocidal composition of Example 2 showed the best performance in this five month modified soil block test, followed by the biocidal composition of Example 1, the biocidal composition of Example 5, then the DDAC treated control and, lastly, the untreated control (as can be seen from Table 3, the untreated controls have no (zero percent) samples in the "no decay" or "questionable" decay categories).

TABLE 4.

SOIL BLOCK EFFICACY TESTING OF QUAT SALTS: PERCENT NO ATTACK  
VERSUS RETENTION.

Biocidal Composition	0.2 pcf (3.2 kg/m <sup>3</sup> )	0.4 pcf (6.4 kg/m <sup>3</sup> )	0.6 pcf (9.6 kg/m <sup>3</sup> )
DDAC	8.3	0.0	16.7
Example 2	37.5	100.0	100.0
Example 5	8.3	16.6	16.7
Example 1	8.3	0.0	33.3

Table 4 clearly shows that the biocidal composition of Example 2 is superior to the other tested biocidal compositions of the present invention, and is far superior to DDAC. It also indicates that the biocidal compositions of Examples 1 and 5 show improved antifungal activity over the DDAC control.

The water leaching data can be used to calculate the remaining biocides in each of the test blocks. The weights or pounds per cubic foot (pcf) of each biocide, as well as the number of moles of biocide or didecyldimethylammonium ion remaining in each test set of blocks can be determined. The calculated pcf and number of moles of didecyldimethylammonium ion for each biocide is given in Table 5 for the 0.2 pcf target retention used for fungal testing and the water leaching test (AWPA E11-87).

TABLE 5

CALCULATED DIDECYLDIMETHYLAMMONIUM ION REMAINING IN WATER  
LEACHED FUNGAL EFFICACY TEST BLOCKS.

Biocidal Composition	Pcf (moles) Remaining
DDAC	0.18 (17 x 10 <sup>-6</sup> )
Example 2	0.19 (14 x 10 <sup>-6</sup> )
Example 5	0.099 (9.0 x 10 <sup>-6</sup> )
Example 1	0.12 (9.7 x 10 <sup>-6</sup> )

A comparison of Table 4 with Table 5 shows that for approximately the same number of moles of the didecyldimethylammonium ions, the biocidal composition of Example 2 is far more effective in fungal testing. In addition, although there remains far less of the biocidal compositions of Examples 1 and 5 than of the DDAC salt, the blocks containing these salts performed as well as the DDAC alone.

In addition, five month fungal cellar testing of various wood preservatives was conducted to determine resistance to brown rot. Southern yellow pine (SYP) Fahlstrom stakes were used for the fungal cellar testing. The Fahlstrom stake is 4 x 38 x 254 mm (0.156 x 1.5 x 10.0 inches) in the tangential, radial, and longitudinal directions, respectively. The stakes were treated with the various chemical treatments according to the AWP "Standard Method of Evaluating Wood Preservatives by Field Tests with Stakes" (E7-93). Post treatment consisted of wet fixation for one week followed by air drying to constant weight. The stakes were placed into tubs (typically 15 x 22 x 26 inches) containing soil obtained from the test plot at Conley, Georgia and was used as is and not sterilized. The moisture content of the soil was maintained at approximately 40 percent throughout the test period. The grading procedure was that described in the AWP E7-93. The results are given below in Table 6, where the following abbreviations are used:

DDAC = Didecyldimethylammonium chloride; and

CCA = chromated copper arsenate.

The loading amounts are in  $\text{lb/ft}^3$ , and the rating is normalized based upon a  $0.440 \text{ lb/ft}^3$  loading of DDAC.

TABLE 6

SALT	RETENTION (pcf)	RATING AWPA E7-93
Biocide Composition of Example 1	0.096	86
	0.181	90
	0.271	96
	0.290	82
	0.594	92
	0.947	92
Biocide Composition of Example 2	0.23	86
	0.43	84
	0.67	92
Biocide Composition of Example 5	0.065	74
	0.128	76
DDAC	0.214	96
	0.440	100
	0.624	98
Boric acid	0.101	0
	0.312	30
	0.496	84
CCA (3 month)	0.086	40
	0.190	74
	0.270	70
	0.391	78
	0.468	94
	0.598	90
Untreated		0

This suggests improved performance resulting from the insoluble nature of these  
 5 biocidal compositions. While not wishing to be bound by any theory, it is believed that the  
 location of the quaternary ammonium ion in the wood matrix is critical to the performance of  
 the biocide. Biocides wherein the quaternary ammonium moiety does not sufficiently  
 penetrate into the substrate matrix are undesirable because of the lack of protection provided  
 to the interior of the substrate, and the increased likelihood of leaching or washing out of the  
 10 biocide due to its proximity to the surface. The compositions of the present invention allow  
 for the delivery of the quaternary ammonium species deep into the substrate matrix, due to its

insolubility in combination with the additional biocide. This insolubility also helps to keep the quaternary ammonium moiety from washing out of the matrix, thereby providing stable, long-term protection of the substrate throughout. Thus, the improved retention of the lipophilic, water insoluble biocides of the present invention results in a better distribution profile of the biocide throughout an impregnated substrate, as well as longer lasting protection in impregnated and coated substrates, particularly when the substrate is to be used in exterior applications, or is to be exposed to contact with aqueous solutions.

### **ANTIMICROBIAL ACTIVITY**

In addition to the antifungal activity against the organisms discussed above, the biocidal compositions of the present invention have also been shown to possess antimicrobial activity against a wide variety of organisms, both fungi and bacteria, including *Staphylococcus aureus*, *Bacillus megaterium*, *Aspergillus niger*, *Pseudomonas aeruginosa*, *Pseudomonas putida*, *Trichoderma viride*, *Phanerochaete chrysosporium*, *Aureobasidium pullulans*, *Penicillium marneffei*, *Rhizopus oryzae*, *Beauveria bassiana*, and *Cunninghamella echinulata* var. *elegans*. In particular, a microemulsion composition containing 20 % of the biocidal composition of Example 2 was prepared as set forth below.

Component	% wt
Biocidal Composition of Example 2	20.00
Ethylene glycol monopropyl ether	55.00
Agsolex-8	10.00
Nonyl phenol 12 mole ETO	15.00
Total	100.00

The ethylene glycol monopropyl ether and Agsolex-8 were first weighed and mixed, and then the nonyl phenol 12 mole ETO was slowly added with constant stirring. The resulting mixture was then heated to 40-45 °C. The biocidal composition of Example 2 was then added slowly to the mixture with stirring until complete dissolution occurred. The mixture was then cooled to room temperature. The resulting 20 % mixture can then be



further diluted by addition of water, and will be stable on dilution at different temperature ranges.

This composition was tested to determine the minimum inhibitory concentration (MIC, the lowest concentration of test substance that completely inhibits growth) against a variety of microorganisms using the agar plate dilution method with an incubation period of 24 to 72 hours.

More specifically, one gram of the 20 % solution discussed above was dissolved in 100 mL of sterile reagent grade water to prepare a 10000 ppm primary stock solution, which was then serially diluted to prepare secondary stock solutions having concentrations of 1000, 100, and 10.0 ppm. Agar media and media broths were autoclaved at 121 °C for 20 minutes prior to use, and stored under aseptic conditions. Appropriate amounts of the secondary stock solutions (2 mL) were mixed with melted agar or broth (18 mL), and the mixtures were poured into Petri dishes and allowed to solidify.

A portion of each inoculum culture was removed and serially diluted to verify the inoculum concentration, and then further diluted, if necessary, to obtain a concentration of  $10^4$  to  $10^6$  organisms per milliliter. Each Petri dish was streaked with  $10^4$  to  $10^6$  cfu/mL of the desired organism. A sterile water control (reagent grade) and solvent control (formulation without active ingredients) were prepared for each test species following the same procedures, except that no test substances were added. Duplicate exposures were prepared for each concentration and control, however, only one replicate per solvent concentration was established. All transfers and inoculations were performed using aseptic techniques.

All tests were conducted on inoculated media that were incubated under conditions suitable for the growth of the test organisms and in the dark. The fungi were maintained in a Millipore incubator at a temperature of  $24 \pm 2$  °C for 48 hours. Bacteria were maintained in a Precision Incubator at a temperature of  $37 \pm 2$  °C for 24 hours. Microbial growth was determined visually at test termination. When a plate was completely clear, or contained a single colony or a barely visible haze, the concentration tested was deemed to be at or above the minimum inhibitory concentration. The microorganisms tested, the test conditions, and the results are set forth below in Table 7.

The test results show that the growth of all organisms was inhibited at 1000 ppm, and *Staphylococcus aureus*, *Bacillus megaterium*, *Pseudomonas putida*, *Trichoderma viride*.

*Phanerochaete chrysosporium*, *Aureobasidium pullulans*, and *Penicillium marneffei* were inhibited at concentrations of 100 ppm and lower. None of the organisms were inhibited by the solvent at 100 ppm, however the solvent was not tested against *Pseudomonas putida*. The test results show that didecyldimethylammonium dimethyldithiocarbamate is inhibitive  
5 against a wide range of microorganisms taken from widely diverse ecological niches.

TABLE 7  
MICROBIOCIDAL ACTIVITY

						Concentration, mg/L						
Microorg. Species	Type	ATCC	Media	Incub. Temp., °C	Replicate	Control	Solvent Control 100 ppm	Solvent Control 1000 ppm	1.0	10	100	1000
<i>S. aureus</i>	bacteria	13273	Nutr. agar	37 ± 1	R1 R2	G	G	-	G	N	N	N
						G	-	G	N	N	N	N
<i>B. megaterium</i>	bacteria	14581	Nutr. agar	37 ± 1	R1 R2	G	G	-	G	G	N	N
						G	-	G	G	N	N	N
<i>A. niger</i>	fungus	16888	Pot. Dextl. agar	26 ± 2	R1 R2	G	G	-	G	G	G	N
						G	-	G	G	G	G	N
<i>P. aeruginosa</i>	bacteria	9027	Nutr. agar	37 ± 1	R1 R2	G	G	-	G	G	G	N
						G	-	G	G	G	G	N
<i>P. putida</i>	bacteria	17484	Nutr. agar	37 ± 1	R1 R2	G	NA	-	G	N	N	N
						G	-	NA	G	N	N	N
<i>Trichodera viride</i>	fungus	16640	Pot. Dextl. agar	26 ± 2	R1 R2	G	G	-	G	G	G	N
						G	-	G	G	G	N	N
<i>Phanerochaete chrysosporium</i>	fungus	24725	Pot. Dextl. agar	26 ± 2	R1 R2	G	G	-	G	G	N	N
						G	-	G	G	N	N	N
<i>Aureobasidium pullulans</i>	fungus	9348	Pot. Dextrose agar	26 ± 2	R1 R2	G	G	-	G	G	N	N
						G	-	G	G	N	N	N

Concentration, mg/L											

G = Growth observed on plate

N = No growth observed on plate

NA = Not applicable

As the above results show, the compositions of the present invention can be used to inhibit, prevent, or control the growth of microorganisms on fibrous materials or surfaces. For instance, the composition according to the present invention can be impregnated into air purification filters. clothing, carpeting, paper products, or other cellulosic or fibrous substrate material, particularly where the substrate material will be exposed to an environment conducive to the growth of microorganisms, or where a microbe-free environment is especially desirable, such as in a healthcare setting. Alternatively, compositions according to the present invention can be impregnated into or coated onto solid surfaces, such as plastic articles for use in a healthcare setting.

These compositions may be applied or impregnated in a form (such as an emulsion) that provides at least about 100 ppm of the biocidal composition, preferably at least about 1000 ppm, of the biocidal composition, to the substrate. For instance, the composition according to Example 2 can be formulated as an emulsion, and then diluted with water until the formulation contains at least 100 ppm of the mixture of the first and second biocidal composition. This formulation can then be impregnated into or coated onto the substrate, and then allowed to dry.

The present invention having been described above, modifications and variations of the present invention will be obvious to those skilled in the art from the foregoing detailed description of the invention. Such modifications and variations are not to be regarded as a departure from the spirit and scope of the invention and are intended to come within the scope of the appended claims.

What is claimed is:

1. A composition comprising a biocidally effective amount of a biocide formed by mixing a first biocidal compound which is a quaternary ammonium salt having the formula



wherein  $R^1$  and  $R^2$  are independently straight, branched, or cyclic alkyl groups 8 to 18 carbon atoms, and  $R^3$  and  $R^4$  are independently straight alkyl groups having 1 to 7 carbon atoms or branched or cyclic alkyl groups having 3 to 7 carbon atoms. and  $X^-$  is an anion and a second biocidal compound selected from the group consisting of alkali and ammonium salts of dialkyldithiocarbamate, monoalkyldithiocarbamate, tetrafluoroborate, and hexafluorophosphate. wherein said composition has a water solubility lower than that of said first biocidal compound.

2. The biocidal composition of claim 1, wherein  $R^1$  and  $R^2$  are alkyl groups having 8 to 12 carbon atoms,  $R^3$  and  $R^4$  are alkyl groups having 1 to 4 carbon atoms. and  $X^-$  is a halogen anion.

3. The biocidal composition salt of claim 2, wherein  $R^1$  and  $R^2$  are both decyl groups and  $R^3$  and  $R^4$  are both methyl groups and said composition has a water solubility lower than that of didecyldimethylammonium chloride.

4. The biocidal composition of claim 3, wherein said dialkyldithiocarbamate is dimethyldithiocarbamate.

5. The biocidal composition of claim 1, further comprising an effective carrier.

6. The biocidal composition of claim 1, further comprising a substrate.

7. The biocidal composition of claim 6, wherein said quaternary ammonium salt is didecyldimethylammonium chloride and said second biocidal compound is sodium dimethyldithiocarbamate.

8. The biocidal composition of claim 6, wherein said substrate is a cellulose-containing material.

9. The biocidal composition of claim 8, wherein said cellulose-containing material is wood.

10. A method for providing a substrate with antifungal or antimicrobial properties, comprising contacting said substrate with the composition according to claim 1 for a period of time and under conditions sufficient to provide said substrate with antifungal or antimicrobial properties.

11. The method of claim 10, wherein  $R^1$  and  $R^2$  are straight, branched, or cyclic alkyl groups having 8 to 18 carbon atoms, and  $R^3$  and  $R^4$  are straight or branched alkyl groups having 1 to 7 carbon atoms.

12. The method of claim 11, wherein said quaternary ammonium salt is didecyldimethylammonium chloride and said second biocide is sodium dimethyldithiocarbamate.

13. The method of claim 10, wherein said contacting comprises a vacuum impregnation, comprising

- (A) placing said substrate in a pressure vessel and evacuating said pressure vessel;
- (B) introducing a treating solution comprising said composition into said pressure vessel under a vacuum, thereby immersing said substrate in said treating solution;
- (C) increasing pressure in said pressure vessel and maintaining said pressure for a treatment time; and

(D) removing treated substrate from said vessel after said treatment time has elapsed.

14. The method of claim 13, wherein said substrate is wood.

15. The method of claim 13, wherein said pressure is increased to about 100 to about 200 psi.

16. The method of claim 13, further comprising again evacuating said pressure vessel after said treatment time has elapsed and prior to removing the treated substrate from the vessel.



# INTERNATIONAL SEARCH REPORT

International Application No.  
PC 1/US 97/13310

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A01N33/12 B27K3/50 B27K3/52 B27K3/34 //(A01N33/12,  
59:26,59:14,47:14)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A01N B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 89 10956 A (ALCO CHEMICAL CORP.) 16 November 1989 see page 4, line 23 - page 6, line 2 see page 8, line 19 - page 10, line 16 see page 15, line 4 - page 18, line 22 see page 22, line 7 - page 23, line 2 see page 26, line 22 - page 28, line 2 see Table I, Example Nos. 2-4, 6-9, 11-14 see claims 1,2,4,18,19 ---	1-12
X	FR 1 058 618 A (CONSORTIUM DE PRODUITS CHIMIQUES ET DE SYNTHÈSE) 17 March 1954 see the whole document ---	1,2,5,6, 8,10,11
X	EP 0 277 556 A (DR. WOLMAN GMBH) 10 August 1988 see column 1, line 21 - column 3, line 13; claims ---	1,5,6, 8-11 1,5,6, 8-11
Y		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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International Application No

PCT/US 97/13310

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